

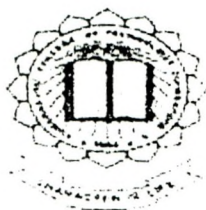


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INHIBITIVE ACTION OF *HIBISCUS CANNABINUS* STEM EXTRACT ON CORROSION OF MILD STEEL IN ACIDIC MEDIA

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ABSTRACT

The influence of stem extract of *Hibiscus cannabinus* on the corrosion of mild steel in 1 M HCl was measured by mass loss method and electrochemical techniques. Results obtained reveal that the stem extract of *Hibiscus cannabinus* act as an effective inhibitor for mild steel in the examined acidic media. Inhibition efficiency was found to increase with increase in concentration of the inhibitor but decrease with rise in temperature. The inhibitive effect could be attributed to the phytochemical constituents present in the inhibitor. The adsorption characteristics of the inhibitor were approximated by Langmuir adsorption isotherm and Temkin adsorption isotherm. Electrochemical measurements confirm mixed mode of inhibition.

Key words: *Hibiscus cannabinus* , corrosion, inhibition, eco-friendly inhibitor

Introduction

The environmental consequences of corrosion on metals are enormous and its inhibition has been deeply investigated. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media¹. The use of naturally occurring substances as inhibitors for metals exposed to acid environment has continued to receive attention as replacement for synthesized organic inhibitors mainly due to its biodegradability and eco-friendliness².

Numerous naturally occurring substances such as natural oil extracted from *Pennyroyal mint*³, *Carica papaya* (seeds, leaves, heart wood and bark)⁴ *Ficus benghalensis* and sprouted seeds of *Phaseolus aureus*^{5,6} *Cyamopsis tetragonaloba*⁷, *Ervatamia coronaria*⁸, *Borassus flabellifer*⁹ have been documented as inhibitors. Due to their biodegradability and eco-friendliness the trend of using these green inhibitors are gaining momentum and in this direction, the present work has been undertaken to study the inhibitive action of stem extract of *Hibiscus cannabinus* (HCS) on the corrosion of mild steel in hydrochloric acid medium.

Materials and methods

Mild steel (MS) specimens of the following chemical composition in weight % - carbon 0.046, manganese 0.548, silicon 0.029 phosphorus 0.012, sulphur 0.019, chromium 0.050, molybdenum 0.015, nickel 0.013, lead 0.003 and Fe 99.265, were used for the entire study. For weight loss study, MS specimens of size 1 x 5 cm² were used. MS specimens with an exposed area of 1 cm² were used for electrochemical study. The specimens were

mechanically polished, degreased, dried and stored in a desiccator.

Preparation of plant extract:

25 g of dried HCS was refluxed with 500 mL of 1 M HCl for 3 hours and kept overnight. The cooled extract was filtered and made up to 500 mL (5% extract).

Weight loss method

Pre weighed test pieces were immersed in triplicate in 100 mL of the solution containing various concentration of the inhibitor and in the absence of inhibitor for a predetermined time period. The test specimens were removed and then washed with de-ionised water, dried and reweighed.

The experiments were performed for various parameters such as:

- Concentration variation (0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%)
- Different time intervals (½ h, 1 h, 3 h, 6 h, 12 h and 24 h)
- Temperature variation (303 K, 313 K, 323 K, 333 K, 338K)

Electrochemical measurement

Potentiodynamic polarisation measurements and Impedance plots were recorded using computerized Solartron model 1284. In this setup a platinum electrode, calomel electrode and MS specimens were used as auxiliary, reference and working electrodes respectively which were immersed in acidic medium in the presence and absence of different concentration of the inhibitor.



Results and discussion:

Effect of concentration of the inhibitor

Table 1 shows the variation of inhibition efficiency with increase in concentration of the inhibitor.

Conc (%)	Immersion Period (Hours)					
	1/2	1	3	6	12	24
0.1	87.8	85.9	75.6	70.68	66.75	55.76
0.2	89.3	86.1	84.7	83.50	71.07	66.09
0.3	89.9	88.7	87.4	84.20	82.96	66.59
0.4	89.9	88.9	88	88.20	84.78	83.39
0.5	91.3	89.4	88.5	87.35	86	84.48
0.6	93.8	92.4	90.9	89.01	88.14	87.5
0.7	94.4	93.1	92.6	90.99	89.7	88.9
0.8	96.9	96.9	95.4	95.74	94.9	94.7

Inspection of the data in the table reveals that as the concentration of the inhibitor increases, the inhibition efficiency also increases. This fact can be attributed to the increased coverage of the inhibitor on the mild steel surface. A maximum of 96.9% IE was observed at 0.8% concentration of the inhibitor.

Impact of immersion time

In order to assess the stability of HCS extract on a time scale, weight loss measurements were performed in 1M HCl in the absence and presence of the inhibitor for various time intervals.

From the Figure 1, it can be seen that as the time of immersion increases, the inhibition efficiency was found to decrease.

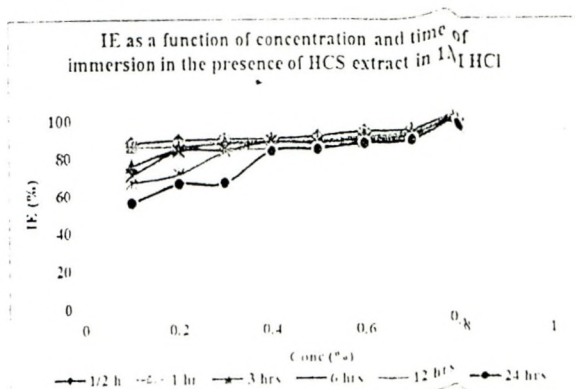


Fig 1 : the variation of IE of the inhibitor with respect to the immersion time.

A maximum IE of 96.9% was maintained till 1 hr and thereafter decreased for longer periods of immersion and then stabilised at 24 h to attain an efficiency of 94.77%. This may be due to the increase in cathodic or hydrogen evolution

kinetic and also due to the increase in the real surface area with time^(10,11)

Temperature effect

To assess the effect of temperature on corrosion and corrosion inhibition processes, mass loss experiments were performed in the temperature range 303-338K in the presence and absence of the HCS extract.

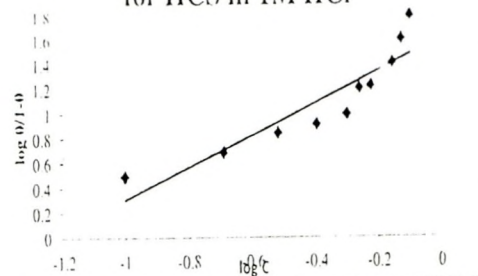
As evident from table 2, the IE increased to attain a maximum of 97.1% at 323K and then declined slightly to furnish an efficiency of 84.4% at 338K. This can be attributed to the fact that most probably the desorption of inhibitor molecules from the metal surface occurs at a faster pace at higher temperature.

Conc. of HCS Extract (%)	IE(%)				
	303K	313K	323K	333K	338K
0.1	87.8	90.3	89.16	39.9	14.8
0.2	89.37	91.2	90.5	68.4	21.7
0.3	89.9	91.5	91.6	83.2	72.9
0.4	89.9	91.5	91.6	73.6	66.9
0.5	91.3	92.67	93.09	86.3	82.3
0.6	93.85	94.3	94.2	90.3	83.6
0.7	94.45	94.6	94.3	90.6	83.8
0.8	96.85	97.1	97.1	92.7	84.4

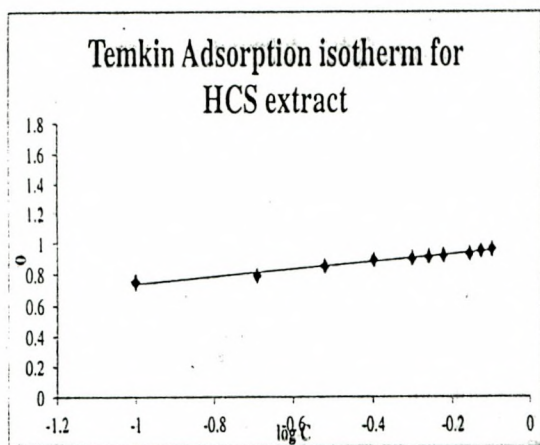
Adsorption kinetics

It is assumed that the inhibition efficiency is comparable to the degree of coverage (θ) of the inhibitor on the metal surface. When the surface of the iron metal is ideally homogenous and there is no interaction among adsorbed species, the adsorption will follow Langmuir isotherm.

Langmuir adsorption isotherm for HCS in 1M HCl



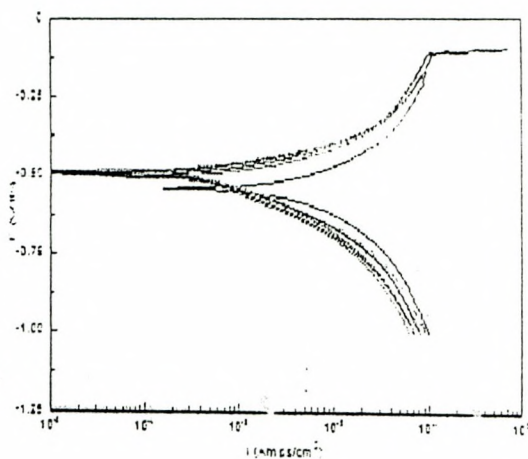
It is clear from the linear plot that the inhibitor follows Langmuir adsorption isotherm. Deviation from unity, as in the present case reveals that there is heterogeneity of the surface and further examination of the data obtained confirms that the inhibitor follows Temkin isotherm, thereby indicating that the behaviour of adsorption is affected by the heterogeneity of the electrode surface^[12].



Polarization behaviour

Figure 3 reflects typical potentiodynamic polarization curves for the mild steel electrodes obtained at 303K in 1M HCl

The results indicate a considerable reduction in the i_{corr} values in the presence of inhibitors. These high values of b_c can be correlated to the decrease of the cathodic transfer



Potentiodynamic polarisation β curves for MS in presence of HCS extract in 1M HCl. Fig 3

coefficient which can be ascribed to the thickening of the electrical double layer due to the adsorbed inhibitor molecules^[13].

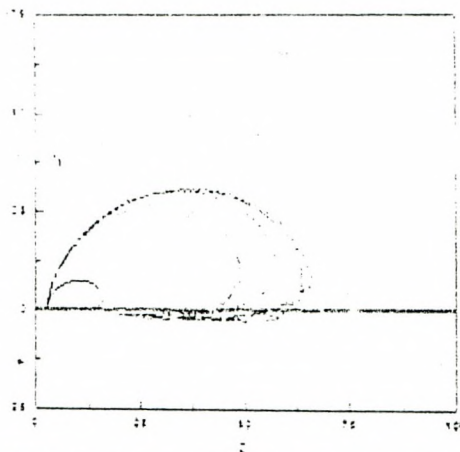
It is found that b_a and b_c values change with respect to blank thereby indicating that the HCS extract reduce the dissolution of metal as well as hydrogen evolution and thus act as mixed type inhibitor.

The increase in I.E. for the inhibitor in HCl media might have been due to the synergistic effect of Cl^- ions (of HCl) adsorbed on the mild steel surface that acted as a main force in the formation of electrostatic bond with the cationic species due to protonation by hydrogen ions of the acid species of the extract which might have probably adsorbed on to the mild steel surface.^[14]

Impedance techniques

The impedance spectral curves of HCS extract in 1M HCl are given in figure

From the figure, it can be observed that they are not perfect semicircle in nature. This can be attributed to the presence of pores on the electrode surface or due to the adsorption of the inhibitor^[15]. Values of R_{ct} and C_{dl} infer that increase in R_{ct} values and decrease in C_{dl} values in the presence of HCS extract. This confirms the adsorption behaviour of HCS extract on MS surface.



Potentiodynamic polarisation and Impedance β curves for MS in presence of HCS extract in 1M HCl. Fig 4





Conclusion

From the above findings, it can be concluded that the HCS extract acts as an effective inhibitor at different environmental condition, the effectiveness can be attributed to the adsorption of the phytochemical constituents of the extract ie, proanthocyanidines on the metal surface and blocking its active sites. The inhibitor used in the current study was found to follow Langmuir and Temkin adsorption isotherm which indicated the monolayer formation with heterogeneity in the surface of the electrode. From electrochemical measurements, it can be seen that the plant extract under investigation behaved as mixed type inhibitor.

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